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Aerosol Acidity Determination by Reaction with 14C Labeled Amine

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Abstract – The acidity of aerosol particles collected on Teflon membrane filters is analyzed by exposure to ^{14}C labelled trimethylamine and by counting the resulting β-ray emission. An accurate calibration is established by the use of known, laboratory-generated sulfuric acid samples. For ambient aerosol samples, results from this new method compare favorably with results from a Gran titration procedure for acidity.

INTRODUCTION

We describe initial progress on a new method to measure the acidity of collected aerosol samples. The method is based upon a technique developed by Huygen (1975) in which sulfuric acid deposits were analyzed by exposure to diethylamine vapor, followed by measurement of the amount of amine that reacted with the deposit. In Huygen's work, the amine was analyzed colorimetrically on aqueous extracts. Our approach is similar, but we expose the aerosol deposits to ^{14}C labeled trimethylamine (TMA) vapor. The amount of TMA that reacts with the sample is determined by measuring its β^- emission intensity. Because the acidity determination can precede other analytical procedures, we can greatly reduce the chance for acidity loss by neutralization with ambient ammonia during such procedures.

EXPERIMENTAL

Aerosol samples were collected on 37 mm dia., 1 μm pore size Teflon membrane filters that were bonded to 2.5 × 2.5 cm square plastic frames (Ghia Corp.*, Pleasanton, CA). Laboratory tests were made using submicron aerosols of sulfuric acid (H_2SO_4) or ammonium sulfate [$(NH_4)_2SO_4$] that were produced using 0.01 N solutions in a nebulizer. The nebulizer was operated with dry, ammonia-free air, and samples were collected at a flow rate of 15 l min^{-1} on 8 cm^2 of area using a filter holder designed to accept the square frames. Several samples of soot from a propane flame were also obtained. Pairs of rural, outdoor samples were collected using two identical dichotomous samplers at Research Triangle Park, NC. Each dichotomous sampler (Model 200, Environmental Research Corp., St. Paul, MN) collected particles in the 0–3.5 and 3.5–20 μm ranges. The inlet of each sampler was equipped with a phosphorous acid coated diffusion denuder to remove ammonia that might otherwise neutralize any collected acidity (Stevens *et al.*, 1978). Liu (1978) has evaluated the diffusion denuder using monodisperse aerosols in the 0.04–1 μm dia. range and found that the losses were less than 3%. Since no loss measurements were made for larger particles, only fine fraction samples (< 3.5 μm) were analyzed in the present work. After collection, the samples were stored in a glass chamber that contained 25 ml of 1.6 N phosphorous acid (H_3PO_3), which produces an ammonia-free atmosphere having a relative humidity above 90%.

At the time of analysis, the samples were inserted into the filter holder of the amine exposure apparatus shown in Fig. 1. An ethanol solution containing a ^{14}C labelled amine was injected onto dry KOH pellets to produce a surge of amine vapor. For most of the results reported here, the ethanol solution consisted of 50 ml of 0.02 N reagent-grade trimethylamine hydrochloride mixed with 50 μCi of ^{14}C labelled trimethylamine hydrochloride obtained from New England Nuclear, Boston, MA. A few measurements, however, were made using methylamine and diethylamine solutions. A repeating dispenser syringe was used to inject from 0.05 to 0.25 ml of solution for each determination. This provided sufficient amine vapor to pass through each sample for a complete reaction. Excess amine vapor was collected in a trap containing charcoal and phosphorous acid to prevent ^{14}C from escaping into the atmosphere.

After exposure to TMA, each sample was positioned next to a detector and counted during four 40 s intervals. The detector was a No. 7231 Geiger Mueller tube (LND, Inc., Oceanside, NY) having a length of 1.2 cm and 2 mg cm^{-2} mica window of 2.8 cm dia. All operations involving ^{14}C were conducted in a hood vented to the outdoors. Before the samples were removed from the hood, the ^{14}C was removed by exposing the samples to high levels of ammonia vapor in a desiccator that contained about 15 ml of concentrated NH_4OH. The TMA is volatilized through an exchange reaction, and the TMA-sulfate compounds are converted to ammonium sulfate. After the samples were made nonradioactive, they were analyzed for elements with atomic numbers in the ranges $13 \leq Z \leq 56$ and $76 \leq Z \leq 82$ using an energy dispersive X-ray fluorescence (XRF) spectrometer designed by Jaklevic *et al.* (1976). The details of the analysis procedure used are described by Dzubay and Rickel (1978) and by Stevens *et al.* (1978).

Samples from one of the replicate sets collected outdoors were not analyzed by the TMA exposure method but were extracted in an aqueous solution and analyzed for H^+, NH_4^+, and SO_4^{2-} ions by Gran titration, ion selective electrode, and spectrophotometric thorin procedures, respectively. These procedures are described by Stevens *et al.* (1978) and are

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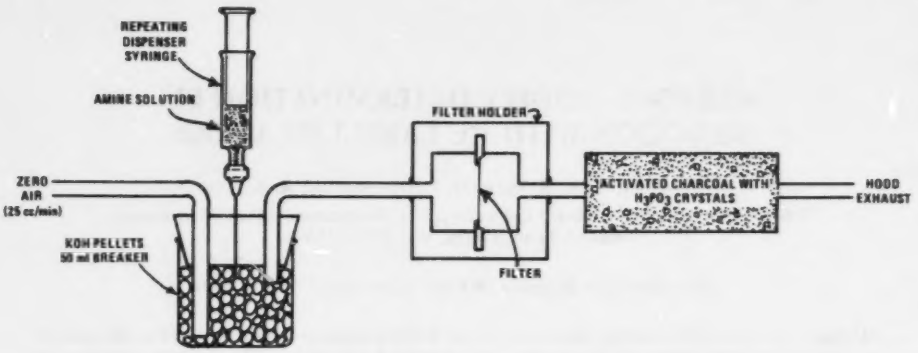

Fig. 1. Amine exposure apparatus.

based upon procedures developed by Brosset and Fern (1978a, b).

RESULTS AND DISCUSSION

Figure 2 shows the response of the TMA exposure method for acidity vs the response of the XRF method for total sulfur for laboratory-generated sulfuric acid deposits. The solid circles represent data on samples stored for 1–120 h in a glass chamber containing 1.6 N phosphorous acid. The open circles represent data on two samples that were stored as above for 130 h followed by storage for an additional 19 and 43 h in a desiccator containing silica gel. Figure 2 shows that acidity can be measured by the TMA method to a precision of about ±15%. The results shown in Fig. 2 were obtained over a three month period; no calibration changes were needed during that time. The intercept is not significantly different from zero, which corresponds to our observation that clean Teflon filters do not absorb appreciable amounts of TMA. The straight line in Fig. 2 is the calibration line that was used in subsequent acidity determinations on unknown samples.

Tests for interferences were made on soot deposits and on ammonium sulfate deposits. The soot deposits, which had mass loadings of 13–16 $\mu g\ cm^{-2}$, produced no detectable response by the TMA exposure method; the upper limit for any sulfuric acid-like response was 0.1 $\mu g\ cm^{-2}$. No response occurred for ammonium sulfate samples that were stored at relative humidities below 50% prior to exposure to TMA. However, when ammonium sulfate samples were stored in a glass chamber containing 1.6 N phosphorous acid (relative humidity above 90%), a slight response occurred such that 20% of the sulfate reacted with TMA and thus appeared as sulfuric acid. Adsorbed moisture was interpreted to be the cause of this response because the interference could be eliminated by transferring the samples from that humid chamber to a dessicator containing dehydrated silica gel before the exposure to TMA. Analysis of stored ammonium sulfate samples for H^+, NH_4^+ and SO_4^{2-} ions showed that such samples were not made acidic during storage in a humid, ammonia-free chamber.

Table 1 shows analytical results for 22 ambient aerosol samples collected at Research Triangle Park, North Carolina during the summer of 1978. For one of the replicate samplers, data are presented for SO_4^{2-}, H^+, and NH_4^- based upon spectrophotometric thorin, Gran titration, and ion selective electrode methods applied to aqueous extracts. For the other replicate sampler, the SO_4^{2-} values shown in Table 1 were calculated from the XRF determinations of sulfur assuming that all of the sulfur occurred as sulfate; the H^+ concentrations were determined by the TMA method.

There is good agreement between methods for SO_4^{2-} and H^+. The mean difference between pairs of sulfate determinations by spectrophotometric thorin and XRF methods is -7 neq m^{-3}, and the standard deviation is 25 neq m^{-3}. The mean difference between pairs of H^+ values determined by Gran titration and TMA methods is -1 neq m^{-3}, and the standard deviation is 21 neq m^{-3}. Such differences are not

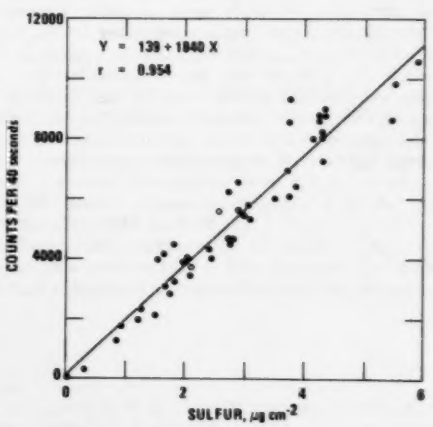

Fig. 2. Response of TMA exposure method vs XRF response for sulfuric acid deposits.

Table 1. Comparative results for SO_4^{2-}, H^+, and NH_4^+ expressed in neq m^{-3} for aerosol particles in the 0–3.5 μm size range*

Sample start date	SO_4^{2-}		H^+		NH_4^+	
	Thorin†	XRF‡	Gran† titration	TMA‡ exposure	Ion† selective electrode	Deduced‡
28.6.78	343	294	132	108	224	186
30.6.78	412	406	157	164	255	241
5.7.78	165	131	82	26	86	105
6.7.78	25	39	13	13	23	26
10.7.78	272	245	96	75	174	170
11.7.78	140	143	48	36	109	107
12.7.78	126	144	43	44	119	100
13.7.78	224	203	99	93	146	110
17.7.78	302	290	146	145	154	144
19.7.78	142	163	40	81	91	83
20.7.78	102	138	0	32	78	105
24.7.78	101	156	20	38	82	118
25.7.78	98	114	22	21	82	93
26.7.78	143	166	53	57	106	109
27.7.78	39	57	12	13	28	44
31.7.78	121	102	29	38	86	64
4.8.78	44	58	5	18	32	40
7.8.78	27	34	0	7	0	27
8.8.78	44	59	0	12	22	47
9.8.78	41	63	43	11	19	52
10.8.78	58	70	0	17	41	53
14.8.78	96	137	56	74	100	63
Mean difference	−7		−1		−1	
Standard deviation	25		21		23	

* Samples collected in two identical dichotomous samplers operated side by side.
† Particles collected in the first sampler.
‡ Particles collected in the second sampler.

significantly different from zero; i.e. the 95% confidence intervals overlap zero.

Table 1 also compares the measured ammonium concentrations with values calculated from the relationship

$$[H^+] + [NH_4^+] = [SO_4^{2-}].$$

The good agreement between the measured and calculated values suggests that H^+, NH_4^+, and SO_4^{2-} are the only ionic species having significant abundances in our samples. A study by Stevens *et al.* (1978) demonstrated that nitrate was insignificant in samples previously collected at our site. Other trace elements in the fine fraction were of minor abundance as indicated by the XRF data in Table 2.

A possible criticism of the present results is that the acidity of the samples may have been altered by our use of a diffusion denuder to remove ammonia during sampling and our subsequent storage of samples in a humid, ammonia-free atmosphere. Brosset (1979) has found that ammonium sulfate samples stored under such conditions undergo a gradual loss of ammonium and gain in acidity. As noted above, we did not see evidence of this when laboratory generated ammonium sulfate samples were first stored and were then analyzed for NH_4^+ and H^+ by ion selective electrode and Gran titration procedures. However, further development and testing of sample storage techniques is obviously needed.

It was observed that the radioactivity of samples exposed to ^{14}C labeled TMA tended to diminish with time as they were stored in room air. We assumed that the radioactivity loss was due to the exchange of ambient ammonia molecules with the TMA in the samples. To test this assumption, we stored a sample in

Table 2. Typical XRF results in μg m^{-3} for samples collected in the fine fraction (< 3.5 μm) at Research Triangle Park, N.C.

Element	Day 198*	Day 222†
Al	0.06	0.04
Si	0.20	0.14
S	4.6	1.1
K	0.06	0.06
Ca	0.04	0.03
Fe	0.12	0.06
Zn	0.03	0.005
Br	0.05	0.02
Pb	0.49	0.10

* A sampling period of 1170 min beginning at 1405 h EDT, 17 July 1978.
† A sampling period of 1402 min beginning at 0924 h EDT, 10 August 1978.

a chamber that contained 100 ppb of ammonia; the radioactivity decreased linearly with time and was completely gone after 3 h. (A second sample that was stored in a plastic bag was fairly stable.) Although this instability of the amine-sulfate compound in the presence of ammonia is not a serious problem for the TMA exposure method described here, it discourages the use of a sulfuric acid sampling technique previously proposed by Snyder *et al.* (1977). In that procedure, an amine vapor was introduced into the sampling stream to react with sulfuric acid to produce a species that had been hoped would be stable in the presence of ammonia or other substances.

Although the results obtained using TMA are most promising, the tests with other amines such as methylamine and diethylamine yielded unsatisfactory results. For methylamine exposures, ammonium sulfate produced a 50–100% interference that we were unable to eliminate. When sulfuric acid samples were exposed to ^{14}C labeled diethylamine, the β^- emission rate diminished rapidly with time if the samples were stored in room air. After counting several of the samples containing diethylamine, the detector became so badly contaminated with radioactivity that the experiments with diethylamine had to be terminated. Presumably, the diethylamine was volatilized from the samples and was then absorbed on the detector window.

CONCLUSIONS

The TMA exposure method appears to be a promising method for analyzing the acidity of collected aerosol samples. The sensitivity can be adjusted to almost any level by adjusting the ratio of ^{14}C to ordinary C atoms in the amine. Further work is needed to determine the optimal method for storing acid samples prior to analysis. Also, the relative responses to H_2SO_4 and NH_4HSO_4 need precise determination, and a more complete study of potential interferences is needed.

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